

## METHOD FOR COATING A SUBSTRATE

**FIELD OF THE INVENTION**

The present invention relates to a method for coating a substrate according to Claim 1, as well as **and** to a coated object according to Claim 8. The preferred. **One** field of application is the coating of components for aircraft turbines or gas turbines, or for garbage incineration plants having temperature-resistant protective layers against high temperature corrosion.

**BACKGROUND INFORMATION**

Components for use in aggressive, hot and corrosive conditions are mostly made of special high temperature alloys based on nickel or cobalt. These alloys are damaged during use, by high temperature corrosion. ~~On account of~~ **Due to** the high temperatures and accelerated by the presence of even the smallest proportions of chlorine and sulfur, nickel and cobalt are converted to their oxides and sulfides. The oxides and sulfides of nickel and cobalt are, however, connected only loosely to the metallic undersurface, and scale off little by little.

It is known that nickel and cobalt alloys, beginning from a certain proportion of aluminum content, have an increased stability against high temperature corrosion. At high temperatures, these alloys develop on their surface a strongly adherent layer of aluminum oxide which regenerates by itself if the layer is damaged. In order to be able to select the base material according to strength criteria, methods for diffusion coating were developed, such as alitizing, by which the base alloy may be enriched retroactively with aluminum in the region near the surface.

An aluminization method is ~~known from US~~ **described in U.S. Patent No. 3,102,044**, in which a layer of aluminum is deposited on the

component part. During the subsequent heat treatment, the aluminum melts and reacts with the substrate to form NiAl.

EP European Published Patent Application No. 0 748 394 B1

5 describes an aluminide coating, enriched with platinum, that is modified with silicon. In order to prepare this layer, in a first step, platinum is deposited on the surface of a nickel superalloy. Subsequently, an aqueous suspension of pulverized elementary aluminum and silicon is applied and dried. Finally the aluminum  
10 is molten, whereupon the silicon dissolves and aluminum atoms and silicon atoms diffuse into the substrate.

Another protective layer against high temperature corrosion is made of MCrAlY (M = Ni, Co; CrAlY = chromium aluminum yttrium).

15 German Published Patent ~~DE~~ Application No. 35 35 548 ~~G2~~ describes a method for preparing a an MCrAlY coating. By galvanic dispersion deposition, a metal matrix is produced of Ni or Co having intercalated particles made of CrAlY. Upon subsequent tempering,  
20 the actual protective layer is then created.

#### SUMMARY

The An example embodiment of the present invention ~~is based on the object of simplifying known methods~~ may provide a simplified method  
25 for producing temperature-resistant protective layers based on aluminum-containing nickel, cobalt and/or platinum layers, and ~~of making~~ may make available an alternative protective layer against high temperature corrosion.

30 This object is attained by the Further aspects and features of the independent claims. Advantageous further developments of the method according to example embodiments of the present invention are described ~~in the dependent claims~~ below.

The subject matter According to an example embodiment of the present invention is, in a method for coating a substrate, in which, ~~in~~ a first step, nickel, cobalt and/or platinum are deposited on a substrate in a deposition bath, ~~known as such~~, without using an external current or electrolytically. In the deposition bath, particles are additionally suspended which contain at least one metal selected from magnesium, aluminum, titanium, zinc, the particles becoming occluded in the coating. ~~Preferably~~ Possibly, but not necessarily, the particles do not include any chromium. In the second step, the actual protective layer against high temperature corrosion is produced by heat treatment.

In the method ~~according to the present invention~~, the reduction of metal salts may take place electrolytically (i.e., by applying an outer current source, or without an external current, ~~that is~~ e.g., by the addition of chemical reducing agents.

In the electrolytic deposition, no chemical reducing agents or their reaction products or decomposition products are present in the deposition bath, that ~~can~~ may be inserted into the metal layer that is created and that ~~can~~ may contaminate it. If, for example, phosphorus-containing compounds are incorporated, phosphides ~~are~~ may be created during the heat treatment which may make the layer brittle, and thereby sensitive.

The higher deposition speed as compared to the reduction without external current ~~is~~ may also be advantageous.

In the case of greatly angular component parts, by deposition using chemical reducing agents, one may achieve the formation of a layer having uniform thickness even at the edges and other surface transition points. In such cases, electrolytic deposition supplies nonuniform layer thicknesses, since the electric field is nonhomogeneous because of shadowing processes.

Besides the usual component parts for an external current-free or electrolytic deposition, particles are suspended in the deposition baths of the method ~~according to the present invention~~ hereof, which contain at least one metal selected from magnesium, aluminum, titanium, zinc, and which are inserted into the metal layer being created.

A spatially uniform insertion of the particles is achieved by a homogeneous distribution of the suspended particles in the deposition bath, which may be ensured by various measures, such as stirring, shaking or the application of ultrasound, etc. Because of the spatially uniform insertion of the particles, it is possible to produce a layer having homogeneous properties. Devices and methods which may be used for this are described, for instance, in GB U.K. Published Patent Application Nos. 1 347 184 A and GB 2 014 189 B.

In the second method step, the coated substrate undergoes heat treatment, ~~preferably~~ e.g., at 600 to 800° C. During this treatment an alloy forms which contains the elements of the external current-free or electrolytically deposited layer and the elements from the particles. In addition, the atoms diffuse from the deposited layer and the particles into the substrate surface, which results in a better adherence of the layer to the substrate.

The quantity ratios of the deposited metals and particles ~~are preferably~~ may be chosen ~~in such a way~~ that stable phases are created. If these ratios are not right, a heterogeneous two-phase mixture forms from an alloy-phase and a pure phase. This mixture demonstrates a somewhat worse resistance to hot gases, since it is attacked by intercrystalline corrosion.

If aluminum-containing particles are used, the heat-treated protective layer contains platinum, nickel aluminide and/or cobalt aluminide which, under high temperature conditions and in the

presence of oxygen, forms aluminum oxide layers that stick to the surface and are resistant to corrosion. The presence of noble metals, such as platinum, in the diffusion layer gives rise to the formation of an oxide layer that is almost fault-free. Aluminum may also be totally or partially replaced by magnesium, titanium or zinc. These metals have the ~~advantageous~~ property that they form well-adhering oxide layers at high temperatures, in the presence of oxygen.

10 The method according to an example embodiment of the present invention may be carried out rapidly, simply and using little expenditure in equipment technology, because the necessary elements, which are required for the formation of the protective layer, are may be able to be applied to the substrate in one working  
15 step.

The protective layer produced by the method according to an example embodiment of the present invention ~~turns~~ may turn out to be so flat that the surface ~~has~~ may have to be touched up very little or not at all. A smooth, aerodynamically favorable surface ~~is very~~ may be important for, e.g., turbine parts, in order to achieve great efficiency.

In ~~one preferred specific~~ an example embodiment of the method  
25 ~~according to the present invention~~, particles are may be used that are made of a single elementary metal.

Elementary, in the ~~sense of the method according to the present invention~~ context, means that the particles used may also have a  
30 thin oxide layer which, because of the non-noble character of magnesium, aluminum, titanium and zinc are created spontaneously under normal environmental conditions, but no additionally applied oxide layer and no additional components.

These particles ~~are~~ may be simple and cost-effective to produce, using ~~known~~ conventional instructions.

In ~~one preferred specific~~ an example embodiment of the method  
5 ~~according to the present invention,~~ particles are may be put in that have an oxide layer which is thicker than the oxide layer formed under normal environmental conditions.

An oxide layer having the thickness mentioned brings on a greatly  
10 improved chemical stability of the particles in acid and basic deposition baths, ~~especially~~ e.g., in the pH range between 4 and 9. The deposition baths used may therefore be used longer before having to be changed.

15 Besides, the use of these chemically more stable particles does not limit the choice of the deposition bath used, since that deposition bath may be selected which supplies the metal layers having the best properties, and the deposition bath does not have to be selected according to whether the particles used in it are  
20 stable.

Magnesium, aluminum, titanium and zinc are non-noble metals which are not stable under acid conditions, but which dissolve as metal ions. Aluminum and zinc also dissolve under basic conditions  
25 because of their amphoteric character, as aluminate or zincate. The solution of the particle in the deposition bath has the effect that interfering foreign substances gradually accumulate in the bath. The baths set for the purpose of an optimal deposition result are toxified in a creeping manner. As a result, the efficiency  
30 of deposition ~~becomes~~ may become worse. In addition, layers that are more and more porous are formed, since the increasing development of hydrogen interferes with the formation of a smooth, uniform layer of high density.

Preferably, ~~the~~ The oxide layer is may be at least twice as thick as the oxide layers that magnesium particles, aluminum particles, titanium particles and zinc particles form spontaneously under normal environmental conditions.

5

~~Investigations have shown that magnesium~~ Magnesium particles, aluminum particles and zinc particles having an oxide layer of at least 0.3  $\mu\text{m}$  in thickness may have an especially good chemical stability.

10

~~Known~~ Conventional methods for producing the oxide layer may be employed. ~~The simplest~~ A simple method is the reaction of the metal particles with hot water. In order to improve the thickness and the density of the oxide layer, inhibiting or complexing additives may be used. Examples are include carbonates, silicates and, phosphates, etc. Oxidizing agents such as persulfate compounds or chromates may also increase the thickness and the density of the oxide layer. Aluminum particles ~~are preferably~~ may be provided with an oxide layer according to the Alrok method, in which sodium carbonate and potassium dichromate are used, or according to the Erftwerk method, in which sodium carbonate, sodium chromate and sodium silicate are used.

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The layer thickness of the oxide skin should be thin enough that the particle receives a sufficient proportion of elementary metal, so that the subsequent formation of an alloy with nickel, cobalt or platinum is not interfered with.

20

~~In one preferred specific~~ an example embodiment of the method ~~according to the present invention,~~ magnesium particles, aluminum particles, titanium particles and/or zinc particles ~~are~~ may be used that are alloyed with nickel, cobalt and/or platinum.

25

These particles ~~have the advantage that they are~~ may be relatively stable in acid and basic deposition baths having a pH value between

3 and 10. As was explained above, one may therefore choose between a greater number of deposition baths.

Furthermore, in this way manner additional components may be introduced for the subsequent alloy formation in the tempering process. This makes possible a still greater freedom of choice in the selection of the deposition bath, since the conditions have to be optimized only for the deposition of a metal.

~~In one preferred specific~~ an example embodiment of the method ~~according to the present invention~~, silicon particles are may additionally be suspended in the deposition bath, which become occluded in the coating.

The heat-treated, silicon-modified layer is more ductile than layers without silicon, and therefore demonstrates a lower tendency to crack formation.

Silicon may also be introduced into the coating by using magnesium particles, aluminum particles, titanium particles and/or zinc particles that are alloyed with silicon.

Besides the quantities used, the ratio in which the particles are inserted into the layer is a function of additional parameters, such as the speed of settling in the deposition bath. In the case of particles that contain alloys, this quantity ratio is established ahead of time. Thereby, the problem arising in connection with using particles made of different materials, ~~namely e.g., of a different rate of insertion, is sidestepped.~~ In ~~a further preferred specific~~ may be avoided. In an example embodiment of the method ~~according to the present invention~~, the layer ~~is~~ may be deposited up to a thickness of 10 to 100  $\mu\text{m}$ , ~~preferably e.g.,~~ 30 to 70  $\mu\text{m}$ .



~~Experiments have shown that layers~~ **Layers** produced using the method according to the present invention, especially hereof, e.g., those having a thickness of 10 to 100  $\mu\text{m}$ , may have excellent corrosion resistance.

In ~~one preferred specific~~ an example embodiment of the method according to the present invention, particles having a diameter of 1 to 50  $\mu\text{m}$ , preferably e.g., 5 to 20  $\mu\text{m}$ , are may be used.

Particles of this size may be suspended in homogeneous distribution in the deposition bath. This fulfills a prerequisite for a spatially uniform insertion of the particles into the deposited layer.

Particles that are smaller than 1  $\mu\text{m}$  tend to aggregation when in suspension, that is, they form clusters. Bigger particles than 50  $\mu\text{m}$ , even when they are able to be suspended homogeneously, which becomes more and more difficult with increasing size, lead to nonuniform spatial distribution of the particle material in the layer, since they are large compared to the layer that has a thickness of 10 to 100  $\mu\text{m}$ . Basically, magnesium-containing, aluminum-containing and titanium-containing particles, because of their lower density, may be selected to be larger than zinc-containing particles.

~~The present invention~~ An example embodiment of the method will be explained in greater detail in the light of the following ~~example,~~ without limiting non-limiting it to this example.

Component parts of a cooling system ~~were~~ are coated so as to be resistant to hot gas corrosion. The component parts, which ~~were~~ are made up of a Ni-based alloy, ~~were~~ are degreased by ultrasound cleaning, ~~were~~ are pickled and provided with a 0.5  $\mu\text{m}$  layer made of strike nickel. Using a galvanic Ni electrolyte, which ~~contained~~ contains particles made of an Al88Si12 alloy having a diameter of

3  $\mu\text{m}$  in a concentration of 10 g/l, a dispersion layer ~~was~~ is deposited. At a current density of 500 A/m<sup>2</sup> and moderate electrolyte motion and component part motion, a layer of a thickness of 30  $\mu\text{m}$  ~~was~~ is applied. By REM measurement (REM =  
5 Rasterelektronenmikroskop (scanning electron microscope)) ~~one was able to show~~ , it may be shown that 25 % by volume of the deposited layer ~~was~~ is made up of AlSi particles. ~~There followed a~~ A two-hour tempering process at 750° C follows for the formation of the desired alloy layer.

Abstract

**ABSTRACT**

~~The present invention relates to~~ In a method for coating a substrate,  
~~as well as to~~ and a coated object. ~~In,~~ in a first step, in an  
5 external current-less or electrolytic manner, nickel and/or cobalt  
and/or platinum are deposited on a substrate in a deposition bath  
~~known per se~~. In the deposition bath, particles are additionally  
suspended which contain at least one metal selected from Mg, Al,  
Ti, Zn and no Cr, the particles becoming occluded in the coating.  
10 In ~~the~~ a second step, the actual protective layer is produced by  
heat treatment. ~~The preferred field of application of the coating~~  
of component parts ~~is~~ may be used for aircraft turbines or gas  
turbines or for garbage incineration systems having  
temperature-resistant protective layers against high temperature  
15 corrosion.